What is claimed is:

1. A method of producing mostly  $5\beta$ , $6\beta$ -epoxides of steroids from  $\Delta^5$ -unsaturated steroids by an epoxidation reaction using a ketone and an oxidizing agent under conditions effective to generate epoxides.

wherein said ketone is selected from compounds of generic formula I.

 $R_1$  or  $R_4$  in formula (I) is selected from alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = alkyl$  or aryl), and halogen;

 $R_2$  or  $R_3$  in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where R<sub>1</sub> or R<sub>2</sub> = H, alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> = alkyl or aryl), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$  or  $R_8$  in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

R<sub>9</sub> or R<sub>10</sub> in formula (I) is selected from alkyl, halogenated alkyl, and aryl; and
A in formula (I) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>.

- 2. The method of claim 1 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.
- 3. The method of claim 2 wherein said epoxidation reaction is carried out using potassium peroxomonosulfate as an oxidizing agent.
- 4. The method of claim 1 wherein said epoxidation reaction is carried out in a homogeneous solvent system containing dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, or a biphasic solvent system containing dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, or mixtures thereof.
- 5. The method of claim 1 wherein said epoxidation reaction is carried out at a temperature within the range from about -10 °C to about 40 °C.
- 6. The method of claim 5 wherein said epoxidation reaction is carried out at room temperature.
- 7. The method of claim 1 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.
  - 8. The method of claim 7 wherein said pH is within the range from about 7.0 to about 7.5.

- 9. The method of claim 7 wherein said pH is controlled by using a pH-stat or a buffer.
- 10. The method of claim 9 wherein said buffer is selected from the solutions consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.
- 11. The method of claim 1 wherein said epoxidation reaction provides said epoxides in at least about 5:1  $\beta/\alpha$ -epoxide ratio.
- 12. A method of producing mostly  $5\beta$ ,  $6\beta$ -epoxides of steroids from  $\Delta^5$ -unsaturated steroids having a substituent at the  $3\alpha$ -position by an epoxidation reaction using a ketone and an oxidizing agent under conditions effective to generate epoxides.
- 13. The method of claim 12 wherein said substituent is selected from OR (where R = H, alkyl or aryl),  $O(CH_2)_nOR$  (where n = 1, 2 or 3, R = H, alkyl or aryl),  $O(CH_2)_mSO_nR$  (where n = 1, 2 or 3; n = 0, 1 or 2; R = H, alkyl or aryl),  $OSiR_1R_2R_3$  (where  $R_1$ ,  $R_2$  or  $R_3 =$  alkyl or aryl),  $OSO_nR$  (where n = 0, 1 or 2; R = H, alkyl or aryl),  $OCO_nR$  (where n = 1 or 2; R = H, alkyl or aryl),  $OCO_nR$  (where n = 1 or 2; R = H, alkyl or aryl),  $OCO_nR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $OPO_nR$  (where where n = 2 or 3; R = alkyl or aryl),  $NR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $NR_1CO_nR_2$  (where n = 1 or 2;  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $NR_1CO_nR_2$  (where n = 1 or 2;  $R_1 = H$ , alkyl or aryl),  $NR_1SO_nR_2$  (where n = 1 or 2;  $R_1 = H$ , alkyl or aryl),  $R_1R_2R_3$  (where  $R_1 = H$ , alkyl or aryl),  $R_1R_2R_3$  (where  $R_1 = H$ , alkyl or aryl),  $R_1R_2R_3$  (where

 $R_1$ ,  $R_2$ , or  $R_3$  = H, alkyl or aryl),  $SiR_1R_2R_3$  (where  $R_1$ ,  $R_2$ , or  $R_3$  = H, alkyl or aryl),  $SO_nR$  (where n = 0, 1 or 2; R = H, alkyl or aryl),  $SCO_nR$  (where n = 1 or 2; R = H, alkyl or aryl), halogen, CN,  $NO_2$ , alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl).

- 14. The method of claim 12 wherein said  $\Delta^5$ -unsaturated steroid having a substituent at the  $3\alpha$ -position is selected from the group consisting of  $\Delta^5$ -unsaturated steroids having a ketal derivative of ketone group or a thicketal derivative of ketone group at the 3-position.
- 15. The method of claim 12 wherein said ketone is selected from the group consisting of compounds of generic formula II, III, IV, and V wherein

$$\begin{array}{cccc}
R_1 & & & & & & & & & \\
R_1 & & & & & & & & \\
R_2 & & & & & & & \\
R_6 & & & & & & & \\
R_6 & & & & & & & \\
R_7 & & & & & & & \\
R_8 & & & & & & & \\
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R_9 & & & & & \\
R_9 & & & & & \\
R_9 & & & & \\$$

 $R_1$ ,  $R_2$ ,  $R_3$ , or  $R_4$  in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSi $R_1R_2R_3$  (where  $R_1$ ,  $R_2$  or  $R_3 = H$ ), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  or  $R_{10}$  in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

A in formula (II) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>;

X in formula (III) is selected from  $(CR_1R_2)_n$  (where n = 1, 2, 3, 4, or 5;  $R_1$  or  $R_2 = H$ , alkyl or aryl), O, S, SO, SO<sub>2</sub>, and NR (where R = H, alkyl or aryl);

 $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , or  $R_{14}$  in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = H$  alkyl or aryl), and halogen;

 $R_{15}$ ,  $R_{16}$ ,  $R_{17}$ , or  $R_{18}$  in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

 $R_{19}$  or  $R_{20}$  in formula (IV) is selected from alkyl, halogenated alkyl, aryl,  $CR_1R_2OCOR_3$  (where  $R_1$ ,  $R_2$  or  $R_3$ = H, alkyl or aryl),  $CR_1R_2OCOOR_3$  (where  $R_1$  or  $R_2$  = H, alkyl or aryl;  $R_3$  = alkyl or aryl),  $CR_1R_2NR_3COOR_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl,  $R_4$  = alkyl or aryl),  $CR_1R_2NR_3COR_4$  (where  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  = H, alkyl or aryl), and  $CR_1R_2NR_3SO_2R_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl;  $R_4$  = alkyl or aryl); and

Y in formula (V) is selected from H, alkyl, halogenated alkyl, aryl, NO<sub>2</sub>, CN, F, Cl, Br, I, COOR (where R = H or alkyl), OR (where R = H, alkyl or aryl), OSO<sub>2</sub>R (where R = H, alkyl or

aryl), OSOR (where R = H, alkyl or aryl), OSR (where R = H, alkyl or aryl), SO<sub>2</sub>R (where R = H, alkyl or aryl), SO<sub>3</sub>R (where R = H, alkyl or aryl), SOON  $R_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), NR<sub>1</sub>SOOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl;  $R_2 =$ alkyl or aryl), NR<sub>1</sub>SOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl), CR<sub>1</sub>R<sub>2</sub>OR<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = H$ , alkyl or aryl), CR<sub>1</sub>(OR<sub>2</sub>)<sub>2</sub> (where  $R_1 = H$  or alkyl;  $R_2 =$ alkyl), CF<sub>3</sub>, CF<sub>2</sub>CF<sub>3</sub>, OTf, OTs, OCOR (where R = H, alkyl or aryl), and OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 =$ alkyl or aryl).

- 16. The method of claim 12 wherein said epoxidation reaction is carried out in a homogeneous solvent system containing dimethoxymethane-acetonitrile-water, acetonitrile-water, acetone-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, or a biphasic solvent system containing dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethylether-water, or mixtures thereof.
- 17. The method of claim 12 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.
- 18. The method of claim 17 wherein said epoxidation reaction is carried out using potassium peroxomonosulfate as an oxidizing agent.
- 19. The method of claim 12 wherein said epoxidation reaction is carried out at a temperature within the range from about -10 °C to about 40 °C.

- 20. The method of claim 19 wherein said epoxidation reaction is carried out at room temperature.
- 21. The method of claim 12 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.
- 22. The method of claim 21 wherein said pH is within the range from about 7.0 to about 7.5.
  - 23. The method of claim 21 wherein said pH is controlled by using a pH-stat or a buffer.
- 24. The method of claim 23 wherein said buffer is selected from the solutions consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, and potassium carbonate, potassium hydroxide, and mixtures thereof.
- 25. The method of claim 12 wherein said epoxidation reaction provides said epoxides in at least about 5:1  $\beta/\alpha$ -epoxide ratio.
- 26. A method of producing mostly  $5\beta$ , $6\beta$ -epoxides of steroids from  $\Delta^5$ -unsaturated steroids by an epoxidation reaction using a dioxirane under conditions effective to generate epoxides,

wherein said dioxirane is selected from compounds of generic formula VI,

 $R_1$  or  $R_4$  in formula (VI) is selected from alkyl, halogenated alkyl, aryl, OR (where R=H, alkyl or aryl), OCOOR (where R=H, alkyl or aryl), OCOOR (where R=H, alkyl or aryl), OCOOCH<sub>2</sub>R (where R=H), OCOOR<sub>1</sub>R<sub>2</sub> (where R=H), or  $R_2=H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3=H$ ), alkyl or aryl), and halogen;

 $R_2$  or  $R_3$  in formula (VI) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where R<sub>1</sub> or R<sub>2</sub> = H, alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> = alkyl or aryl), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$  or  $R_8$  in formula (VI) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

R<sub>9</sub> or R<sub>10</sub> in formula (VI) is selected from alkyl, halogenated alkyl, and aryl; and A in formula (VI) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>.

27. The method of claim 26 wherein said dioxirane is generated in situ from a ketone and an oxidizing agent selected from potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

wherein said ketone is selected from compounds of generic formula I,

 $R_1$  or  $R_4$  in formula (I) is selected from alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = alkyl or aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = alkyl$  or aryl), and halogen;

 $R_2$  or  $R_3$  in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R=H, alkyl or aryl), OCOOR (where R=H, alkyl or aryl), OCOOR (where R=H), OCOOCH<sub>2</sub>R (where R=H), OCOOR<sub>1</sub>R<sub>2</sub> (where R=H), or  $R_2=H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3=H$ ), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$  or  $R_8$  in formula (I) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

R<sub>9</sub> or R<sub>10</sub> in formula (I) is selected from alkyl, halogenated alkyl, and aryl; and A in formula (I) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>.

- 28. The method of claim 26 wherein said epoxidation reaction is carried out in a solvent selected from acetonitrile, dimethoxymethane, acetone, dioxane, dimethoxyethane, tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, diethylether, water, and mixtures thereof.
- 29. The method of claim 26 wherein said epoxidation reaction is carried out at a temperature within the range from about -40 °C to about 40 °C.

- 30. The method of claim 26 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.
- 31. The method of claim 26 wherein said epoxidation reaction provides said epoxides in at least about 5:1  $\beta/\alpha$ -epoxide ratio.
- 32. A method of producing mostly  $5\beta$ , $6\beta$ -epoxides of steroids from  $\Delta^5$ -unsaturated steroids having a substituent at the  $3\alpha$ -position by an epoxidation reaction using a dioxirane under conditions effective to generate epoxides.
- 33. The method of claim 32 wherein said substituent is selected from OR (where R = H, alkyl or aryl),  $O(CH_2)_nOR$  (where n = 1, 2 or 3, R = H, alkyl or aryl),  $O(CH_2)_mSO_nR$  (where n = 1, 2 or 3; n = 0, 1 or 2; R = H, alkyl or aryl),  $OSiR_1R_2R_3$  (where  $R_1$ ,  $R_2$  or  $R_3 =$  alkyl or aryl),  $OSO_nR$  (where n = 0, 1 or 2; R = H, alkyl or aryl),  $OCO_nR$  (where n = 1 or 2; R = H, alkyl or aryl),  $OCO_nR$  (where where n = 2 or 3; R = alkyl or aryl),  $OCONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $OPO_nR$  (where where n = 2 or 3; R = alkyl or aryl),  $OCONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $OCO_nR_2$  (where n = 1 or 2;  $R_1$  or  $R_2 = H$ , alkyl or aryl),  $OCO_nR_2$  (where n = 1 or 2;  $OCONR_2R_3$  (where  $OCONR_2R_3$  (where  $OCONR_3R_3$  (where  $OCONR_3R_3$

- 34. The method of claim 32 wherein said  $\Delta^5$ -unsaturated steroid having a substituent at the  $3\alpha$ -position is selected from the group consisting of  $\Delta^5$ -unsaturated steroids having a ketal derivative of ketone group or a thicketal derivative of ketone group at the 3-position.
- 35. The method of claim 32 wherein said dioxirane is selected from the group consisting of compounds of generic formula VII, VIII, IX and X.

$$\begin{array}{c|c}
R_2 & -O \\
R_1 & R_3 \\
R_6 & + R_7 \\
R_5 & R_9 & R_{10}
\end{array}$$

$$\begin{array}{c|c}
R_3 \\
R_7 \\
R_8
\end{array}$$

$$\begin{array}{c|c}
VII \\
R_8
\end{array}$$

 $R_1$ ,  $R_2$ ,  $R_3$ , or  $R_4$  in formula (VII) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOCH<sub>2</sub>R (where R = H, alkyl or aryl), OCOOCH<sub>2</sub>R (where R = H, alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = H$ , alkyl or aryl), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  or  $R_{10}$ , in formula (VII) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and CONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

A in formula (VII) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>;

X in formula (VIII) is selected from  $(CR_1R_2)_n$  (where n = 1, 2, 3, 4, or 5;  $R_1$  or  $R_2 = H$ , alkyl or aryl), O, S, SO, SO<sub>2</sub>, and NR (where R = H, alkyl or aryl);

 $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , or  $R_{14}$  in formula (VIII) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOOR (where R = H)

or aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = alkyl$  or aryl), and halogen;

 $R_{15}$ ,  $R_{16}$ ,  $R_{17}$ , or  $R_{18}$  in formula (VIII) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

 $R_{19}$  or  $R_{20}$  in formula (IX) is selected from alkyl, halogenated alkyl, aryl,  $CR_1R_2OCOR_3$  (where  $R_1$ ,  $R_2$  or  $R_3$ = H, alkyl or aryl),  $CR_1R_2OCOOR_3$  (where  $R_1$  or  $R_2$  = H, alkyl or aryl;  $R_3$  = alkyl or aryl),  $CR_1R_2NR_3COOR_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl,  $R_4$  = alkyl or aryl),  $CR_1R_2NR_3COR_4$  (where  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  = H, alkyl or aryl),  $CR_1R_2NR_3SO_2R_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl;  $R_4$  = alkyl or aryl); and

Y in formula (X) is selected from H, alkyl, halogenated alkyl, aryl, NO<sub>2</sub>, CN, F, Cl, Br, I, COOR (where R = H or alkyl), OR (where R = H, alkyl or aryl), OSO<sub>2</sub>R (where R = H, alkyl or aryl), OSOR (where R = H, alkyl or aryl), SO<sub>2</sub>R (where R = H, alkyl or aryl), SO<sub>3</sub>R (where R = H, alkyl or aryl), SOON  $R_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), NR<sub>1</sub>SOOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl;  $R_2 =$ alkyl or aryl), NR<sub>1</sub>SOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl;  $R_2 =$ alkyl or aryl), CR<sub>1</sub>R<sub>2</sub>OR<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = H$ , alkyl or aryl), CR<sub>1</sub>(OR<sub>2</sub>)<sub>2</sub> (where  $R_1 = H$  or alkyl;  $R_2 =$ alkyl), CF<sub>3</sub>, CF<sub>2</sub>CF<sub>3</sub>, OTf, OTs, OCOR (where R = H, alkyl or aryl), and OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 =$ alkyl or aryl).

36. The method of claim 32 wherein said dioxirane is generated in situ from a ketone and an oxidizing agent selected from potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

37. The method of claim 36 wherein said ketone is selected from the group consisting of compounds of generic formula II, III, IV, and V,

$$\begin{array}{c|c}
R_1 & O \\
R_1 & R_2 & R_3 \\
R_6 & + R_7 \\
R_5 & R_1 & R_8
\end{array}$$

$$\begin{array}{c}
R_7 & A & \\
R_8 & R_{10} & R_{10} & R_{10} \\
\end{array}$$
II

 $R_1$ ,  $R_2$ ,  $R_3$ , or  $R_4$  in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOOR (where R = H, alkyl or aryl), OCOOR (where R = aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1$ ,  $R_2$  or  $R_3 = alkyl$  or aryl), and halogen;

 $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$  or  $R_{10}$  in formula (II) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

A in formula (II) is selected from halogen, OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>;

X in formula (III) is selected from  $(CR_1R_2)_n$  (where n=1, 2, 3, 4, or 5;  $R_1$  or  $R_2=H$ , alkyl or aryl), O, S, SO, SO<sub>2</sub>, and NR (where R=H, alkyl or aryl);

 $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ , or  $R_{14}$  in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, OR (where R = H, alkyl or aryl), OCOR (where R = H, alkyl or aryl), OCOR (where R = H) or

aryl), OCOOCH<sub>2</sub>R (where R = aryl), OCONR<sub>1</sub>R<sub>2</sub> (where R<sub>1</sub> or R<sub>2</sub> =H, alkyl or aryl), OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where R<sub>1</sub>, R<sub>2</sub> or R<sub>3</sub> = alkyl or aryl), and halogen;

 $R_{15}$ ,  $R_{16}$ ,  $R_{17}$ , or  $R_{18}$  in formula (III) is selected from H, alkyl, halogenated alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

 $R_{19}$  or  $R_{20}$  in formula (IV) is selected from alkyl, halogenated alkyl, aryl,  $CR_1R_2OCOR_3$  (where  $R_1$ ,  $R_2$  or  $R_3$ = H, alkyl or aryl),  $CR_1R_2OCOOR_3$  (where  $R_1$  or  $R_2$  = H, alkyl or aryl;  $R_3$  = alkyl or aryl),  $CR_1R_2NR_3COOR_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl,  $R_4$  = alkyl or aryl),  $CR_1R_2NR_3COR_4$  (where  $R_1$ ,  $R_2$ ,  $R_3$  or  $R_4$  = H, alkyl or aryl),  $CR_1R_2NR_3SO_2R_4$  (where  $R_1$ ,  $R_2$  or  $R_3$  = H, alkyl or aryl;  $R_4$  = alkyl or aryl); and

Y in formula (V) is selected from H, alkyl, halogenated alkyl, aryl, NO<sub>2</sub>, CN, F, Cl, Br, I, COOR (where R = H or alkyl), OR (where R = H, alkyl or aryl), OSO<sub>2</sub>R (where R = H, alkyl or aryl), OSOR (where R = H, alkyl or aryl), SO<sub>2</sub>R (where R = H, alkyl or aryl), SO<sub>2</sub>R (where R = H, alkyl or aryl), SOON  $R_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl), NR<sub>1</sub>SOOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl;  $R_2 =$ alkyl or aryl), NR<sub>1</sub>SOR<sub>2</sub> (where  $R_1 = H$ , alkyl or aryl;  $R_2 =$ alkyl or aryl), CR<sub>1</sub>R<sub>2</sub>OR<sub>3</sub> (where  $R_1, R_2$  or  $R_3 = H$ , alkyl or aryl), CR<sub>1</sub>(OR<sub>2</sub>)<sub>2</sub> (where  $R_1 = H$  or alkyl;  $R_2 =$ alkyl), CF<sub>3</sub>, CF<sub>2</sub>CF<sub>3</sub>, OTf, OTs, OCOR (where R = H, alkyl or aryl), and OSiR<sub>1</sub>R<sub>2</sub>R<sub>3</sub> (where  $R_1, R_2$  or  $R_3 =$ alkyl or aryl).

- 38. The method of claim 32 wherein said epoxidation reaction is carried out in a solvent selected from acetonitrile, dimethoxymethane, acetone, dioxane, dimethoxyethane, tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, diethylether, water and mixtures thereof.
- 39. The method of claim 32 wherein said epoxidation reaction is carried out at a temperature within the range from about -40 °C to about 40 °C.
- 40. The method of claim 32 wherein said epoxidation reaction is carried out at a pH within the range from about 7.0 to about 12.0.
- 41. The method of claim 32 wherein said epoxidation reaction provides said epoxides in at least about 5:1  $\beta/\alpha$ -epoxide ratio.

## 42. A method comprising:

producing mostly  $5\beta$ , $6\beta$ -epoxides of steroids by epoxidation reactions of  $\Delta^5$ -unsaturated steroids of generic formula XI catalyzed by ketones of generic formula XII, wherein

$$R_1$$
 $H$ 
 $R_2$ 
 $R_3$ 
 $R_4$ 
 $R_5$ 
 $R_7$ 
 $R_7$ 

 $X_1$  in formula (XI) is selected from H, OR (where R = H or alkyl), OCH<sub>2</sub>OCH<sub>3</sub>, OCOR (where R =alkyl or aryl), OSiR<sub>1</sub>'R<sub>2</sub>'R<sub>3</sub>' (where R<sub>1</sub>', R<sub>2</sub>' or R<sub>3</sub>' = alkyl or aryl), halogen, CN, alkyl, aryl, and COOR (where R = H, alkyl or aryl);

 $R_1$  in formula (XI) is selected from H, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OCH<sub>2</sub>OCH<sub>3</sub>, halogen, CF<sub>3</sub>, and CF<sub>2</sub>CF<sub>3</sub>;

 $R_2$  and  $R_3$  in formula (XI) are each selected from the group consisting of H, alkyl, aryl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OSiR<sub>1</sub>'R<sub>2</sub>'R<sub>3</sub>' (where R<sub>1</sub>', R<sub>2</sub>' or R<sub>3</sub>' = alkyl or aryl), COR (where R = alkyl), COCH<sub>2</sub>OR (where R = H or alkyl), COCH<sub>2</sub>OCOR (where R = alkyl or aryl), COCH<sub>2</sub>F, COOR (where R = H or alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)R (where R = alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>OR (where R = H or alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>OCOR (where R = alkyl or aryl), and C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>F; or, are selected from the group consisting of O, OCH<sub>2</sub>CH<sub>2</sub>O, and OCH<sub>2</sub>CH<sub>2</sub>O;

 $R_4$  in formula (XI) is selected from H,  $C_1$ – $C_4$  alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and  $OSiR_1'R_2'R_3'$  (where  $R_1'$ ,  $R_2'$  or  $R_3'$  = alkyl or aryl);

 $R_5$  in formula (XI) is selected from H,  $C_1$ – $C_4$  alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and  $OSiR_1$ ' $R_2$ ' $R_3$ ' (where  $R_1$ ',  $R_2$ ' or  $R_3$ ' = alkyl or aryl);

 $R_6$  in formula (XI) is selected from H, halogen, OR (where R = H or alkyl), and OCOR (where R =alkyl or aryl);

 $R_7$  in formula (XI) is selected from H, halogen, OR (where R = H or alkyl), and OCOR (where R =alkyl or aryl);

$$R_{19}$$
 $+$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{18}$ 
 $R_{15}$ 
 $R_{16}$ 
 $R_{16}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 
 $R_{10}$ 

R<sub>15</sub> and R<sub>16</sub> in formula (XII) are each selected from alkyl and aryl;

 $R_{17}$  and  $R_{18}$  in formula (XII) are each selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

 $R_{19}$  and  $R_{20}$  in formula (XII) are each selected from  $C_1-C_4$  alkyl, halogenated alkyl, and halogen; and

A in formula (XII) is selected from OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>.

- 43. The method of claim 42 wherein said  $C_1$ – $C_4$  alkyl is selected from the group consisting of methyl, ethyl, normal-propyl, iso-propyl, normal-butyl, iso-butyl, sec-butyl, and tert-butyl; and said aryl selected from the group consisting of phenyl, substituted phenyl, naphthyl, and substituted naphthyl groups.
- 44. The method of claim 42 wherein said epoxidation reactions are carried out in a homogeneous solvent system selected from the group consisting of dimethoxymethane-acetonitrile-water, acetonie-water, dioxane-water, dimethoxyethane-water, tetrahydrofuran-water, and mixtures thereof.
- 45. The method of claim 42 wherein said epoxidation reactions are carried out in a biphasic solvent system selected from the group consisting of dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethyletherwater, and mixtures thereof.
- 46. The method of claim 42 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.

- 47. The method of claim 42 wherein said epoxidation reactions are carried out at a temperature within the range from about -10 °C to about 40 °C.
- 48. The method of claim 47 wherein said epoxidation reactions are carried out at room temperature.
- 49. The method of claim 42 wherein said epoxidation reactions are carried out at a pH within the range from about 7.0 to about 12.0.
  - 50. The method of claim 49 wherein said pH is within the range from 7.0 to 7.5.
  - 51. The method of claim 49 wherein said pH is controlled by using a pH-stat or a buffer.
- 52. The method of claim 51 wherein said buffer is selected from the group consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.

## 53. A method comprising:

producing mostly  $5\beta$ , $6\beta$ -epoxides of steroids by epoxidation reactions of  $\Delta^5$ -unsaturated steroids of generic formula XIII catalyzed by ketones of generic formula XIV, XV, XVI, and XVII, wherein

$$X_{2}$$
 $X_{3}$ 
 $X_{14}$ 
 $X_{14}$ 
 $X_{10}$ 
 $X_{10}$ 
 $X_{11}$ 
 $X_{11}$ 
 $X_{12}$ 
 $X_{11}$ 
 $X_{11}$ 

 $X_2$  in formula (XIII) is selected from the group consisting of H, OR (where R = H or alkyl), OCH<sub>2</sub>OCH<sub>3</sub>, OCOR (where R =alkyl or aryl), OSiR<sub>1</sub>'R<sub>2</sub>'R<sub>3</sub>' (where R<sub>1</sub>', R<sub>2</sub>' or R<sub>3</sub>' = alkyl or aryl), halogen, CN, alkyl, aryl, and COOR (where R = H, alkyl or aryl), and,

 $X_3$  in formula (XIII) is selected from the group consisting of OR (where R = H or alkyl), OCH<sub>2</sub>OCH<sub>3</sub>, OCOR (where R = alkyl or aryl), OSiR<sub>1</sub>'R<sub>2</sub>'R<sub>3</sub>' (where R<sub>1</sub>', R<sub>2</sub>' or R<sub>3</sub>' = alkyl or aryl), halogen, CN, NO<sub>2</sub>, alkyl, and aryl; or,

X<sub>2</sub> and X<sub>3</sub> in formula (XIII) are selected from the group consisting of O, OCH<sub>2</sub>CH<sub>2</sub>O, and OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O;

 $R_8$  in formula (XIII) is selected from H, OR (where R = H or alkyl), OCOR (where R = A alkyl or aryl), OCH<sub>2</sub>OCH<sub>3</sub>, halogen, CF<sub>3</sub>, and CF<sub>2</sub>CF<sub>3</sub>;

 $R_9$  and  $R_{10}$  in formula (XIII) are each selected from the group consisting of H, alkyl, aryl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), OSiR<sub>1</sub>'R<sub>2</sub>'R<sub>3</sub>' (where R<sub>1</sub>', R<sub>2</sub>' or R<sub>3</sub>' = alkyl or aryl), COR (where R = alkyl), COCH<sub>2</sub>OR (where R = H or alkyl), COCH<sub>2</sub>OCOR (where R = alkyl or aryl), COCH<sub>2</sub>F, COOR (where R = H or alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)R (where R = alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>OR (where R = H or alkyl), C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>OCOR (where R = alkyl or aryl), and C(OCH<sub>2</sub>CH<sub>2</sub>O)CH<sub>2</sub>F; or R<sub>9</sub> and R<sub>10</sub> in formula (XIII) are selected from the group consisting of O, OCH<sub>2</sub>CH<sub>2</sub>O, and OCH<sub>2</sub>CH<sub>2</sub>O;

 $R_{11}$  and  $R_{12}$  in formula (XIII) are each selected from the group consisting of H,  $C_1$ – $C_4$  alkyl, halogen, OR (where R = H or alkyl), OCOR (where R = alkyl or aryl), and  $OSiR_1$ ' $R_2$ 'R<sub>3</sub>' (where  $R_1$ ',  $R_2$ ' or  $R_3$ ' = alkyl or aryl);

 $R_{13}$  and  $R_{14}$  in formula (XIII) are each selected from the group consisting of H, halogen, OR (where R = H or alkyl), and OCOR (where R = alkyl or aryl);

$$\begin{array}{ccc}
 & & & & & \\
R_{19} & & & & & \\
 & & & & & \\
R_{17} & & & & & \\
R_{16} & & & & & \\
\end{array}$$

$$\begin{array}{cccc}
 & & & & & \\
R_{18} & & & & \\
R_{18} & & & & \\
\end{array}$$

$$\begin{array}{cccc}
 & & & & & \\
R_{18} & & & & \\
\end{array}$$

$$\begin{array}{ccccc}
 & & & & \\
R_{18} & & & & \\
\end{array}$$

R<sub>15</sub> or R<sub>16</sub> in formula (XIV) is selected from alkyl and aryl;

 $R_{17}$  or  $R_{18}$  in formula (XIV) is selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2$  = H, alkyl or aryl);

 $R_{19}$  or  $R_{20}$  in formula (XIV) is selected from H,  $C_1$ – $C_4$  alkyl, halogenated alkyl, and halogen; and

A in formula (XIV) is selected from OTf, BF<sub>4</sub>, OAc, NO<sub>3</sub>, BPh<sub>4</sub>, PF<sub>6</sub>, and SbF<sub>6</sub>;

$$R_{23}$$
 $R_{24}$ 
 $R_{21}$ 
 $R_{22}$ 
 $R_{22}$ 
 $R_{22}$ 
 $R_{22}$ 

Y in formula (XV) is selected from CH<sub>2</sub>, O, S, SO, SO<sub>2</sub>, and NR (where R = H or alkyl);

 $R_{21}$  or  $R_{22}$  in formula (XV) is selected from H, alkyl, aryl, COOR (where R = H, alkyl or aryl), and  $CONR_1R_2$  (where  $R_1$  or  $R_2 = H$ , alkyl or aryl);

 $R_{23}$  or  $R_{24}$  in formula (XV) is selected from H, halogen,  $C_1$ – $C_4$  alkyl, halogenated alkyl, and OCOR (where R = alkyl or aryl);

$$R_{25}$$
  $R_{26}$   $XVI$ 

 $R_{25}$  or  $R_{26}$  in formula (XVI) is selected from  $C_1$ – $C_4$  alkyl, halogenated alkyl,  $CH_2OCOR$  (where R = alkyl or aryl); and

Z in formula (XVII) is selected from H,  $C_1$ – $C_4$  alkyl, aryl,  $NO_2$ , CN, F, Cl, Br, I, COOR (where R = alkyl),  $CH_2OR$  (where R = H or alkyl),  $CH(OR)_2$  (where R = alkyl),  $CF_3$ ,  $CF_2CF_3$ , OTf, OTs, OCOR (where R = alkyl or aryl), and  $OSiR_1'R_2'R_3'$  (where  $R_1'$ ,  $R_2'$  or  $R_3'$  = alkyl or aryl).

- 54. The method of claim 53 wherein said  $C_1$ – $C_4$  alkyl is selected from the group consisting of methyl, ethyl, normal-propyl, iso-propyl, normal-butyl, iso-butyl, sec-butyl, and tert-butyl; and said aryl selected from the group consisting of phenyl, substituted phenyl, naphthyl, and substituted naphthyl groups.
- 55. The method of claim 53 wherein said epoxidation reactions are carried out in a homogeneous solvent system selected from the group consisting of dimethoxymethane-acetonitrile-water, acetonie-water, dioxane-water, dimethoxyethane-water, and tetrahydrofuran-water, and mixtures thereof.
- 56. The method of claim 53 wherein said epoxidation reactions are carried out in a biphasic solvent system selected from the group consisting of dichloromethane-water, chloroform-water, benzene-water, toluene-water, dimethoxymethane-water, or diethyletherwater, and mixtures thereof.

- 57. The method of claim 53 wherein said oxidizing reagent is selected from the group consisting of potassium peroxomonosulfate, sodium hypochlorite, sodium perborate, hydrogen peroxide, and peracids.
- 58. The method of claim 53 wherein said epoxidation reactions are carried out at a temperature within the range from about -10 °C to about 40 °C.
- 59. The method of claim 58 wherein said epoxidation reactions are carried out at room temperature.
- 60. The method of claim 53 wherein said epoxidation reactions are carried out at a pH within the range from about 7.0 to about 12.0.
  - 61. The method of claim 60 wherein said pH is within the range from 7.0 to 7.5.
  - 62. The method of claim 60 wherein said pH is controlled by using a pH-stat or a buffer.
- 63. The method of claim 62 wherein said buffer is selected from the group consisting of sodium bicarbonate, sodium carbonate, sodium borate, sodium hydrogenphosphate, sodium dihydrogenphosphate, sodium hydroxide, potassium hydrogenphosphate, potassium dihydrogenphosphate, potassium bicarbonate, potassium carbonate, potassium hydroxide, or mixtures thereof.